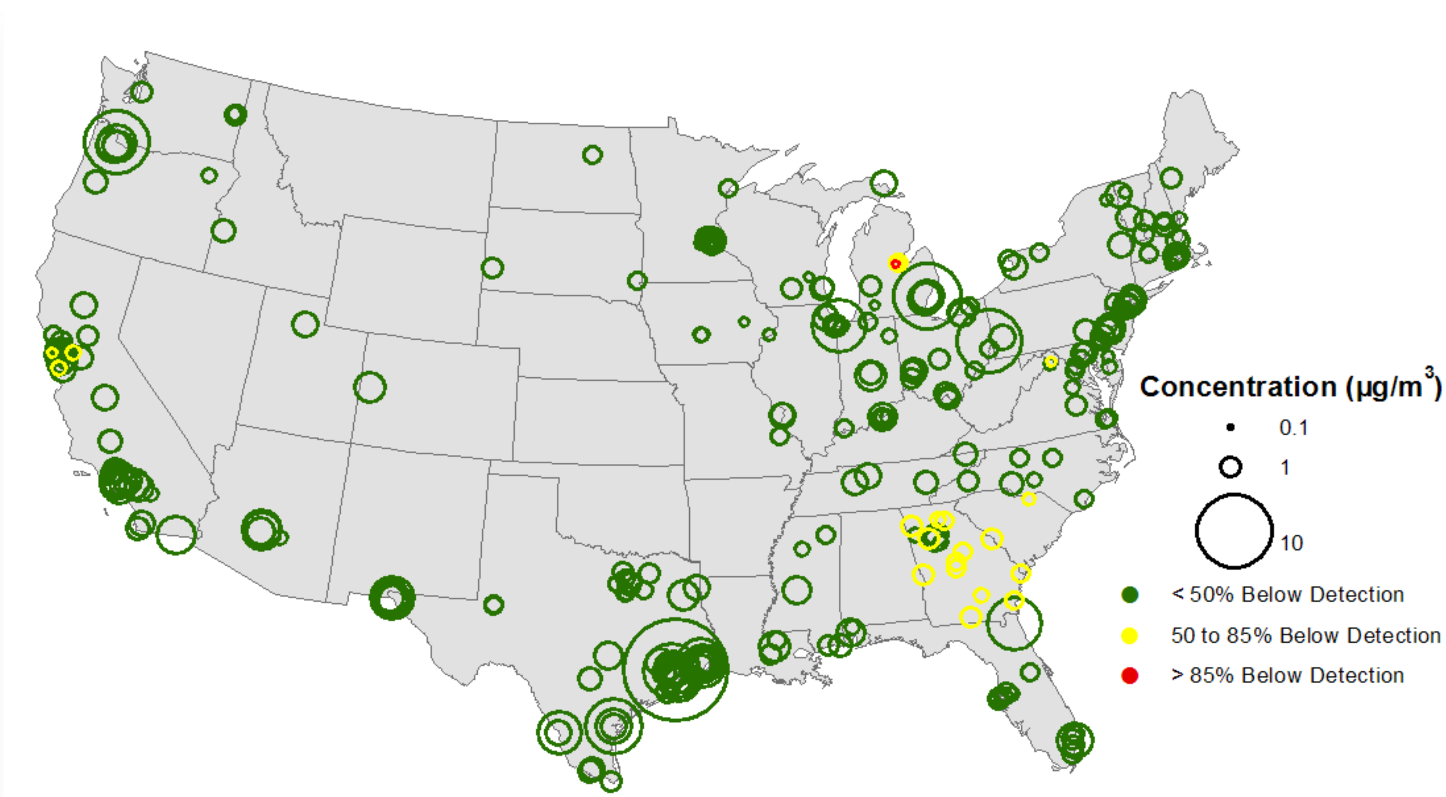
Characterizing Air Toxics



With only a few exceptions, ambient benzene concentrations are above detection limits across the country.

Sonoma Technology, Inc.

Analysis Flow Chart – Theory

Set Project Goals

Design Monitoring Study

Data Quality Objectives (DQOs)

Perform Monitoring and Analysis

Data Preparation and Validation

Data Analysis

Communication and Action

Overview

- Using spatial and temporal characterizations of air toxics data, we can improve our understanding of emissions and the atmospheric processes that influence pollutant formation, distribution, and removal.
- Goals of these data analyses can include
  - Identifying possible important sources of air toxics.
  - Determining chemical and physical processes that lead to high air toxics concentrations.

Suggested Analyses

Questions	Examples of Analyses
What is the nature and extent of air toxics problems in your area?	
Considering risk, what are the most important air toxics at each site?	Determine median concentrations and concentration ranges and compare to appropriate risk levels
How do these species vary by measurement season, month, and time of day? Are findings consistent with national level results?	Prepare box plots of concentrations by season, month, and time of day; compare to national results and expectations based on local conditions
Do species show any day-of-week patterns?	Prepare box plots of concentrations by day of week; compare results to expected patterns of local emissions
How do concentrations compare to other locations, risk levels, remote background, or reference concentrations?	Compare monitor-level data to national-perspective plots

Suggested Analyses

Questions	Examples of Analyses
What are local sources of air toxics?	
What are the potential air toxics sources in the area?	Investigate Google map of area; overlay criteria pollutant and air toxics emission inventory information
Do the air toxics corroborate the source mixture?	• Examine key species noted as tracers for the expected sources in the area using scatter plots and correlation matrices • Compare concentrations of air toxics and nontoxic tracer species to further assess sources (e.g., $PM_{2.5}$ components, hydrocarbons)

Data-Driven Analysis

- Are data of sufficient type (and associated uncertainty), quantity, and quality to meet project objectives with statistical certainty?
  - Uncertainty – sampling, analytical, representativeness
  - Quantity – are there enough samples?
  - Data quality – contamination and other data issues
- Using the data
  - Evidence-based comparison to initial hypothesis
  - Accept or reject initial hypothesis, or find inconclusive results regarding the initial hypothesis

Interpreting Results

Using the data to test project hypotheses

- Health effects assessment
  - Compare concentrations to health benchmarks
  - Compare concentrations to those at other sites, cities, states, nation
  - Identify pollutants whose concentrations are above health benchmarks
- Community baseline
  - Characterize annual averages, seasonal variability
  - Quantify toxics concentrations likely to be targeted by emissions reductions measures
  - Characterize spatial variability
- Methods evaluation
  - Is method more accurate, precise, sensitive?
  - Does it have better time resolution?
  - How much does it cost versus routine method?

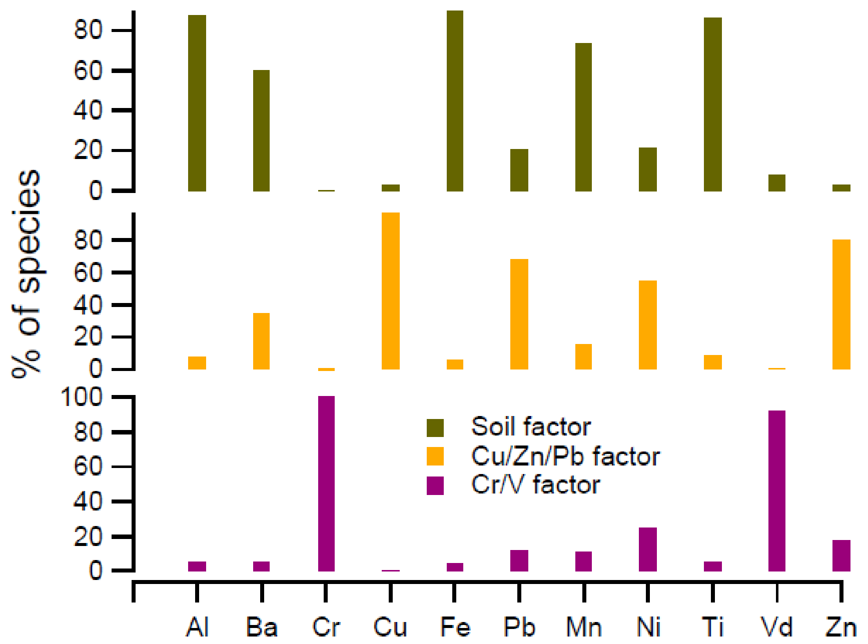
Emissions Source Type Characteristics

Understand emissions source types of air toxics to help develop a conceptual model of concentration patterns and gradients that might be expected.

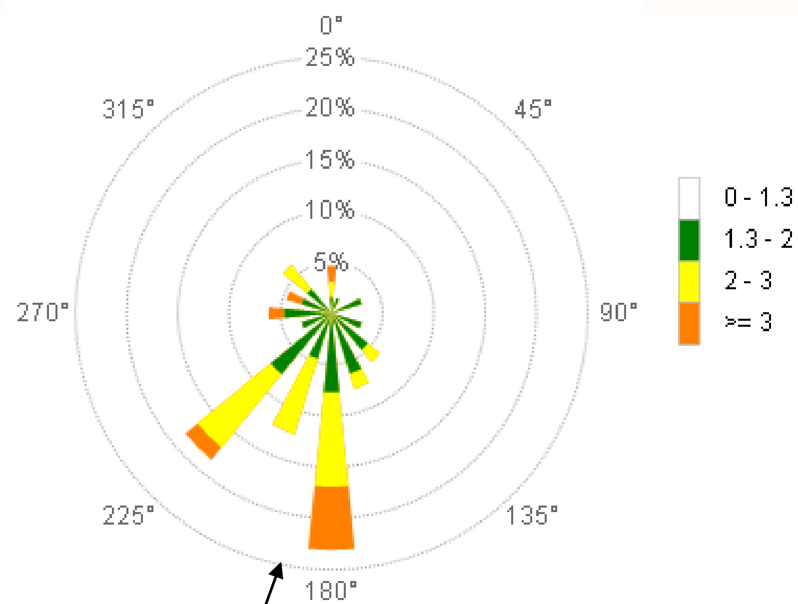
- **Major source emissions**, for example, are a localized (point) source of toxics and may show steep concentration gradients.
- **Area source emissions** are typically well-distributed emissions sources because there are multiple sources in an area.
- **Mobile source air toxics** exhibit both point source and area source characteristics.

Emissions Source Type Characteristics

Chemical Source Profiles

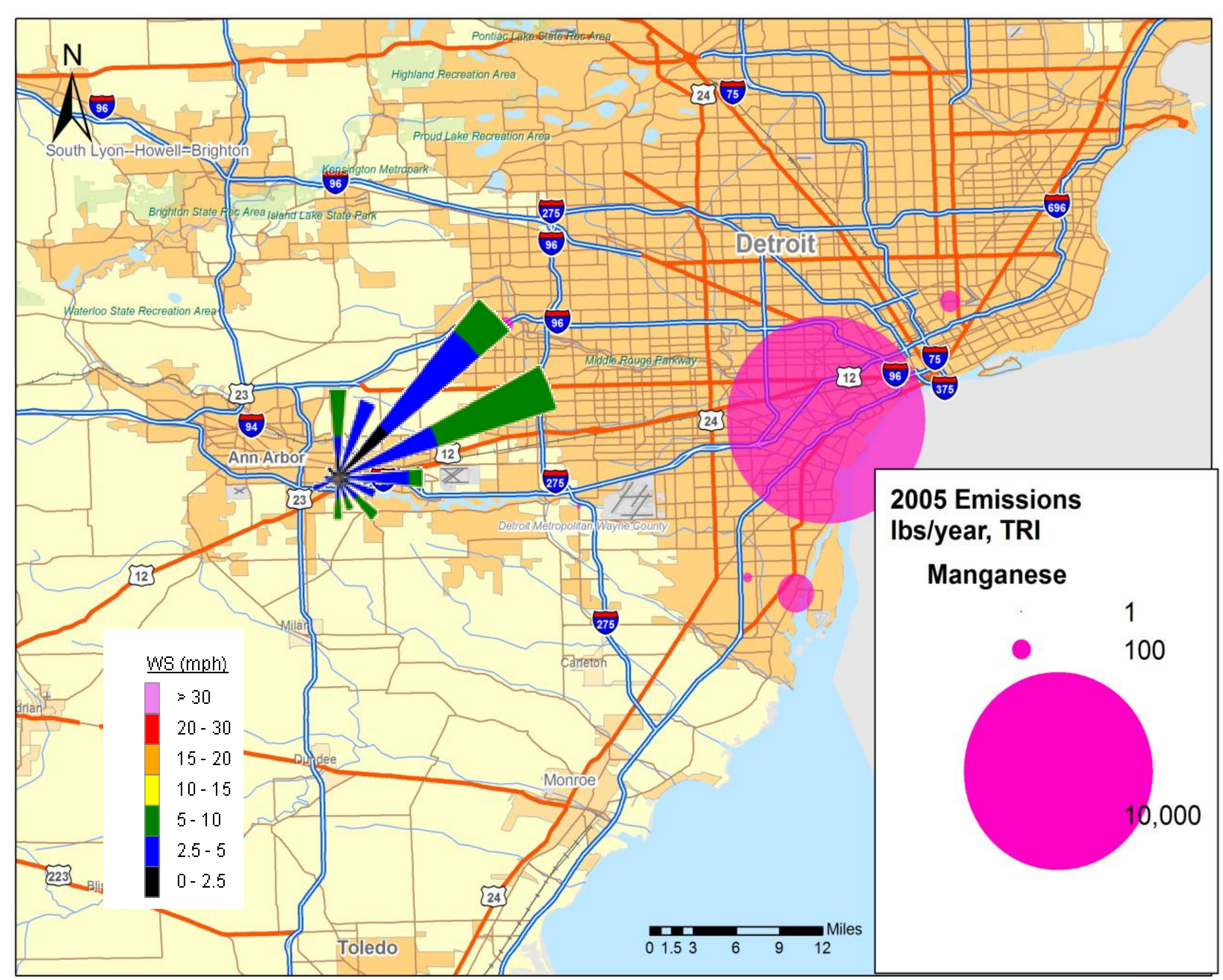


Pollution Rose



Concentrations are high when winds blow from the south

Emissions Source Type Characteristics



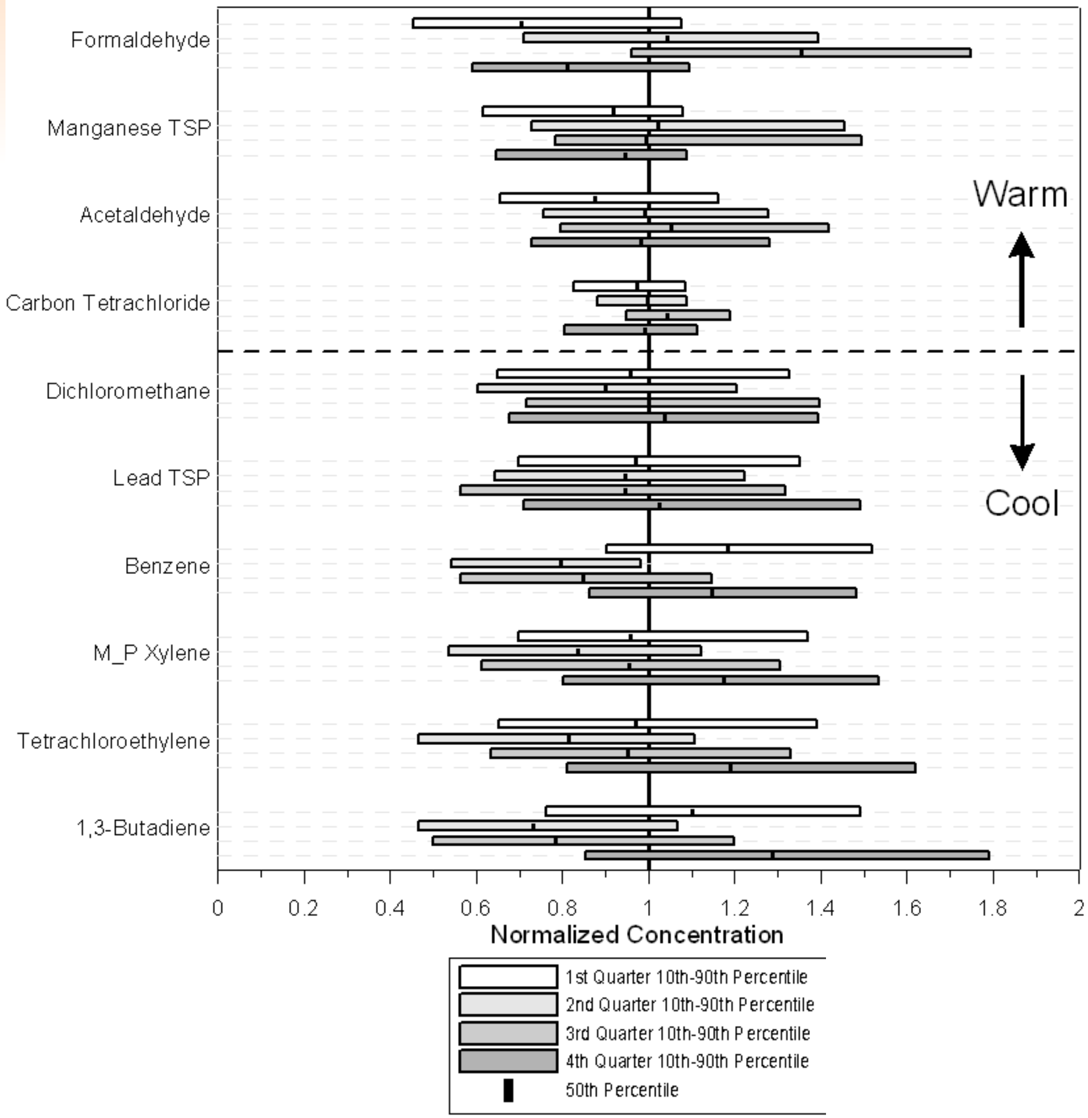
Source apportionment: wind roses for high zinc/manganese (Zn/Mn) factor/source days at Detroit's Allen Park site point to large point sources in the industrial area of Detroit.

Seasonal Patterns
Conceptual Model

- Cool season expectations
  - Mixing heights are lower in cold months. Low mixing heights reduce the amount of air available for pollutant dispersion, which results in higher ambient concentrations of pollutants.
  - Temperatures are lower and sunlight is reduced in cold months. This combination can lead to a reduction in evaporative emissions (e.g., gasoline) and reduced photochemistry. Reductions in temperature and sunlight also limit formation of hydroxyl radicals, which efficiently oxidize many air toxics.
  - Typically more precipitation occurs during winter months and reduces dust emissions.
- Warm season expectations
  - Mixing heights are higher in warm months, allowing more dilution and transport of air toxics which, in turn, reduces ambient concentrations.
  - Higher temperatures and increased sunlight in warm months lead to an increase in evaporative emissions and photochemistry.
  - Conditions are typically drier, producing more dust.
  - Wildfire activity can also cause an increase in concentrations of pollutants emitted in smoke.

Seasonal Patterns
A National Perspective

- To help place site data in perspective, national seasonal patterns are shown: the 10th, 50th, and 90th percentiles of national 2003–2005 normalized seasonal concentrations for selected pollutants by calendar quarter.
- Parameters at the top of the figure have peak concentrations in the warm season, while those at the bottom have peaks in the cool season.
- Warm season peaks are likely due to secondary photochemical production and dust; it is unclear why carbon tetrachloride shows a warm season peak.
- Cool season peaks are primarily due to lower mixing heights in the winter.



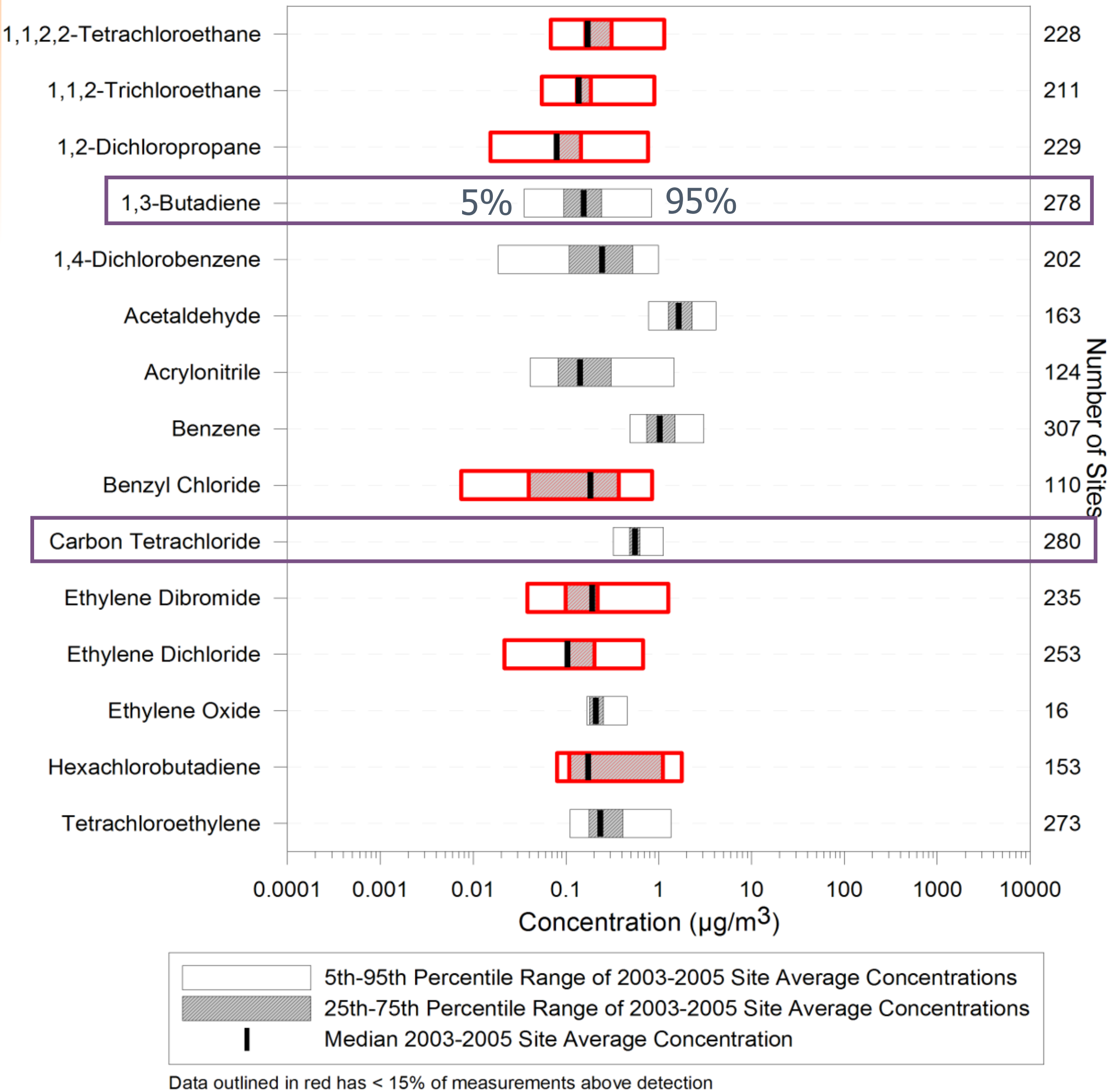
Spatial Comparisons

Are concentrations at the site of interest

- statistically significantly higher than other sites (mean, median, other metric)?
- higher when the wind is from a certain direction?
- higher than concentrations at other sites in the community, state, and/or nation?
- higher than expected, given local population and emissions sources?

Note: Higher could be lower if the focus is on clean sites.

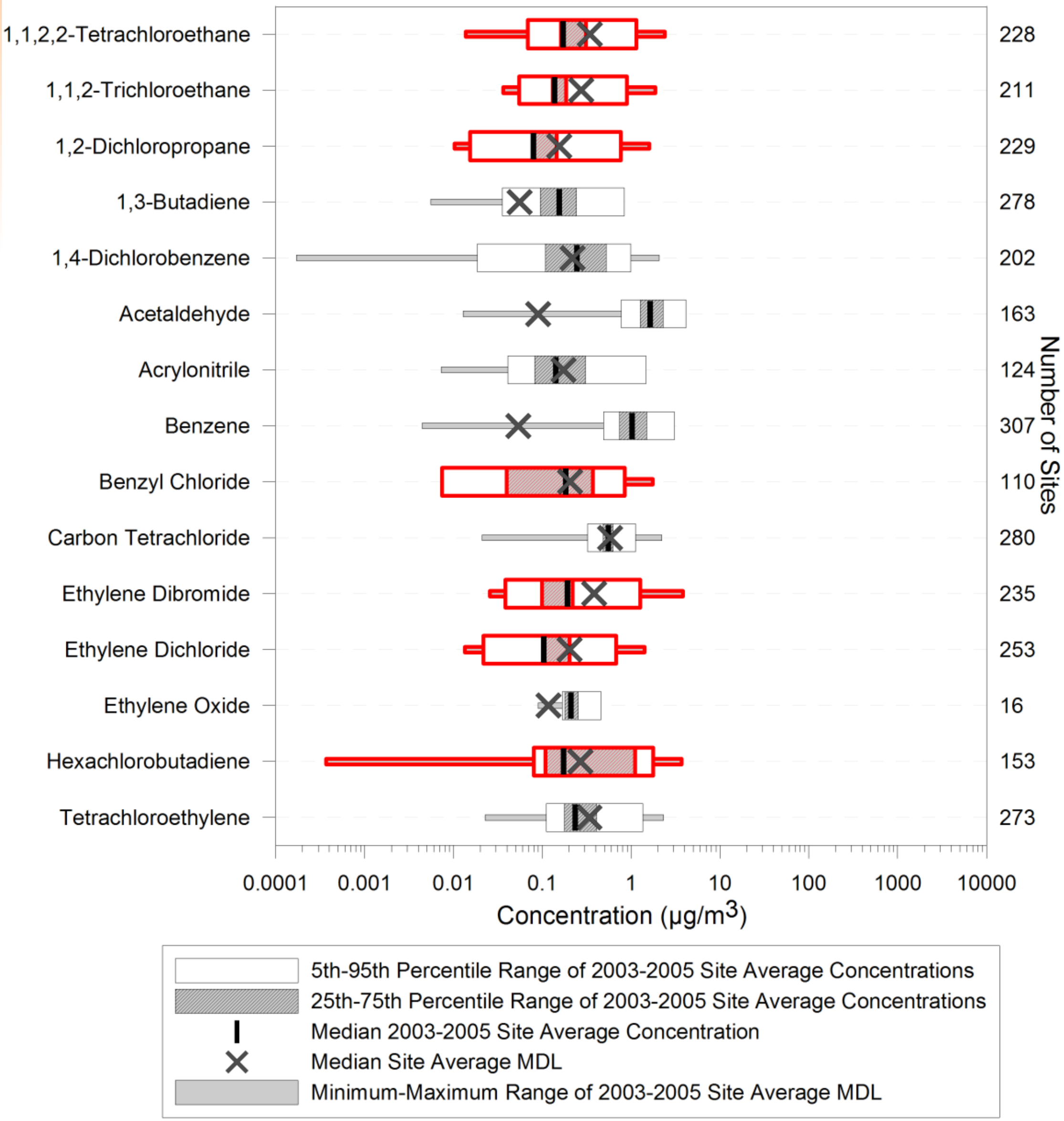
National Concentration Ranges



Interpretation

- Summary plots provide an overview of the spatial variability of, and a comparison within and between, air toxics. Spatial variability is represented by the width of the bar—nationally, air toxics concentrations typically varied by a factor of 3 to 10.
- 1,3-butadiene concentrations show high spatially variability (due to its relatively high reactivity).
- Carbon tetrachloride shows less spatial variability due to its low removal rate from the atmosphere and the absence of domestic emissions.
- A table of national concentration summary statistics can be found in the appendix to *Preparing Data for Analysis*, Data Analysis Workbook, Section 4.

National Concentration Ranges

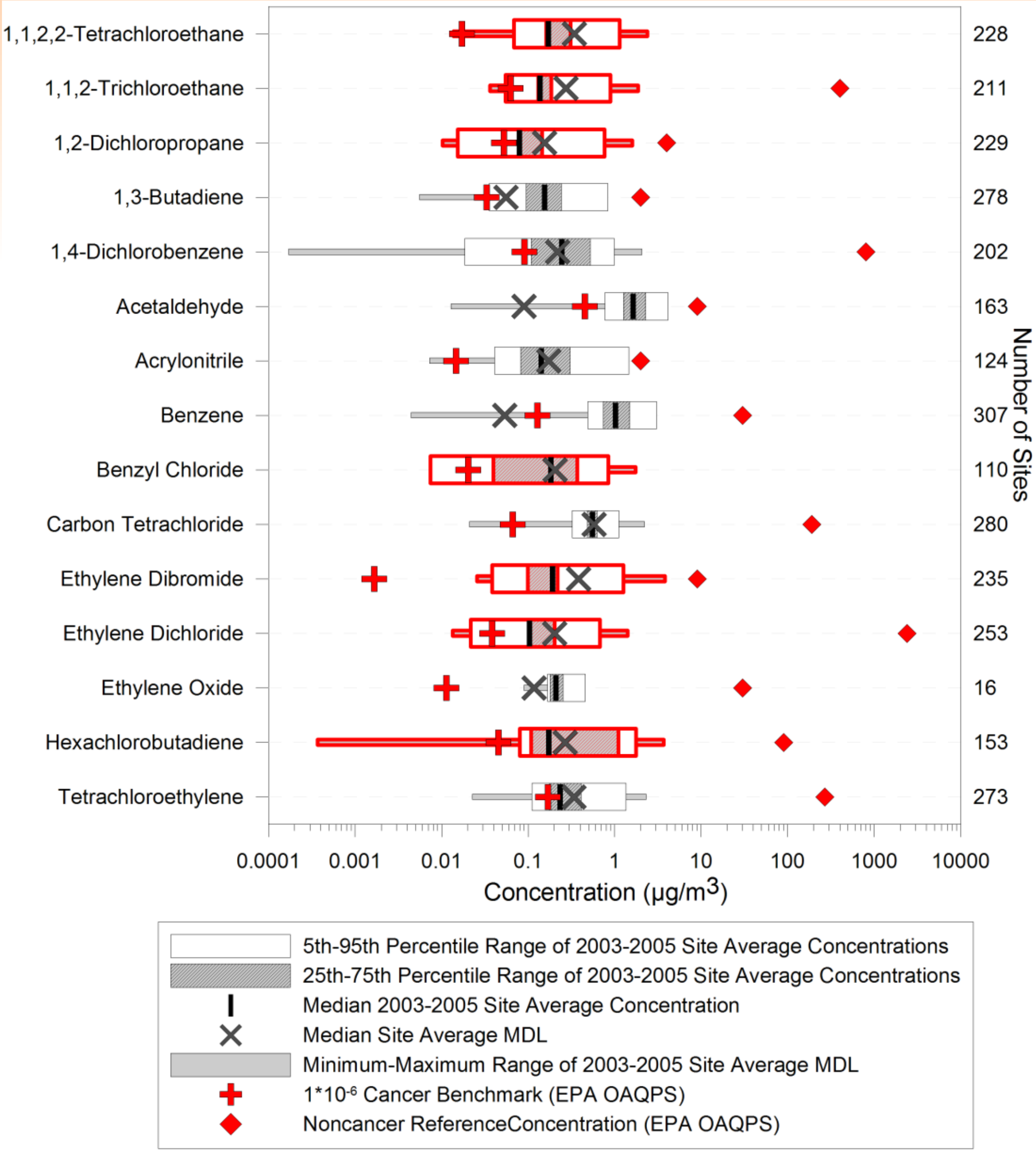


Data outlined in red has < 15% of measurements above detection

Adding MDLs

- MDL ranges (thin lines) and median MDLs (the X marks) illustrate how well pollutants are monitored.
- The minimum-maximum range of MDL concentrations and the median MDL concentration for a 2003–2005 site average are shown.
- The median concentration of the pollutants outlined in red are always below the median MDL. These pollutants are not adequately monitored in the national ambient monitoring networks (i.e., only a few sites have >15% of data above detection).

National Concentration Ranges

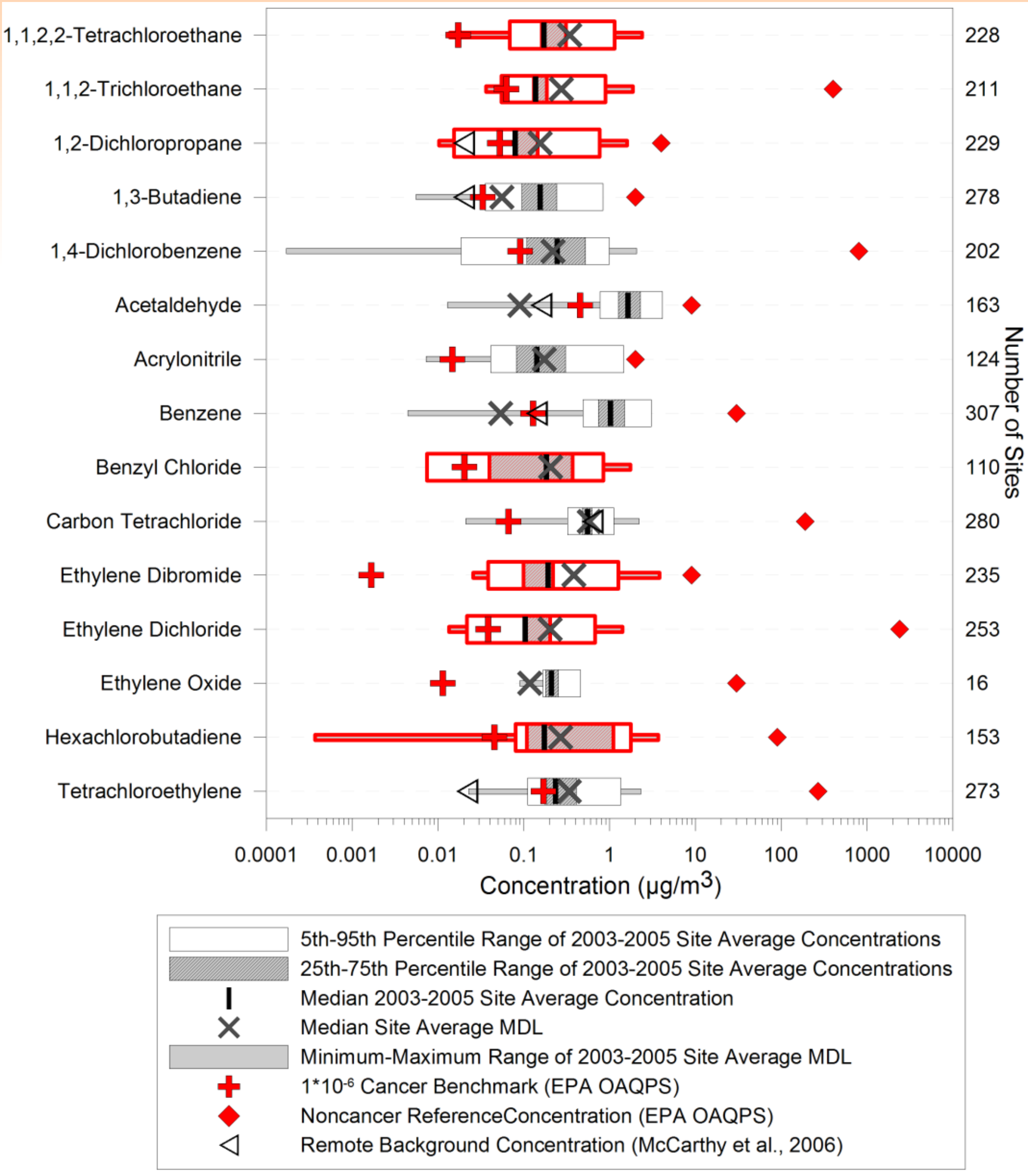


Data outlined in red has < 15% of measurements above detection

Risk Levels

- Chronic exposure concentration associated with a 1-in-a-million cancer risk (+) and noncancer reference concentrations (♦) are used to show a relationship to human health.
- National measured annual average air toxics concentrations are usually above the chronic exposure concentration associated with a 1-in-a-million cancer risk (+) and below noncancer reference (♦) concentrations.
- Pollutant concentration ranges outlined in red may actually be below levels of concern, but the data are not resolved well enough to characterize risk.

National Concentration Plots



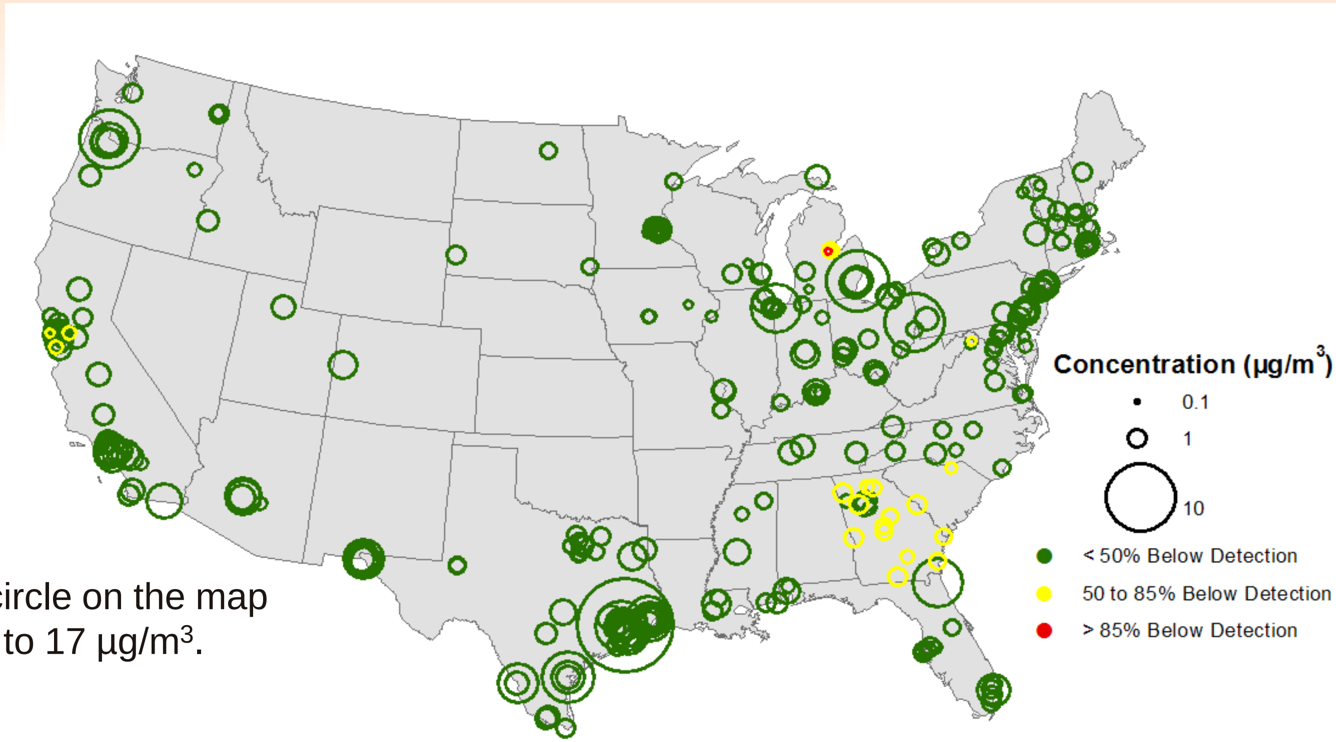
Data outlined in red has < 15% of measurements above detection

Remote Background

- Remote background concentrations (◁) show the lowest levels expected to be seen in the remote atmosphere; urban concentrations of most air toxics should not typically fall below this value.
- As expected, most air toxics are factors of 5 to 10 above their remote background concentrations, with the exception of carbon tetrachloride – the only air toxic dominated by background concentrations.
- Background estimates are provided for about 40 air toxics (see *Preparing Data for Analysis*, Data Analysis Workbook, Section 4).

Spatial Patterns – Maps

Benzene Concentrations 2003–2005

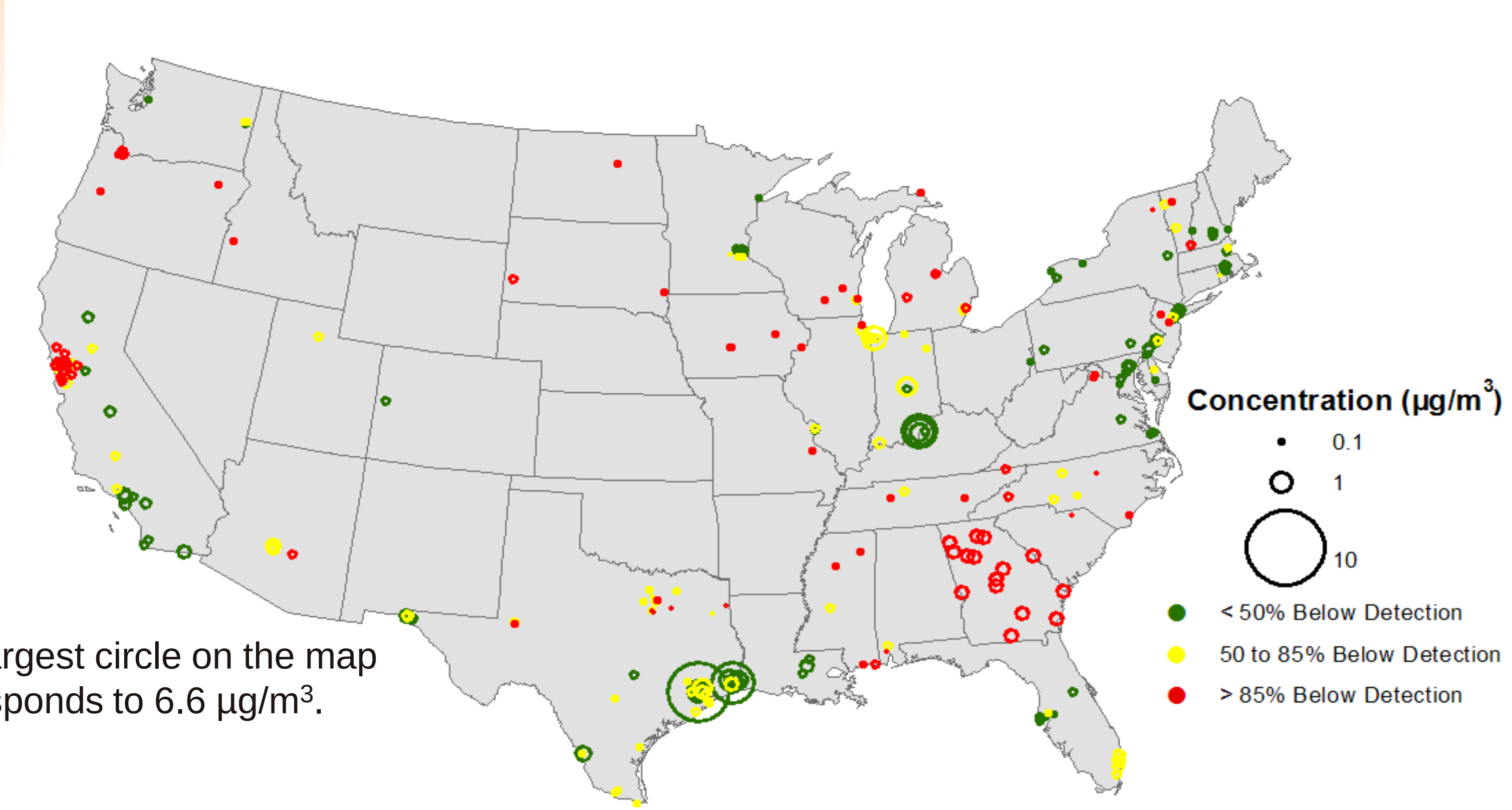


The largest circle on the map corresponds to 17 µg/m³.

- With only a few exceptions, ambient benzene concentrations are above detection across the country (i.e., 0% to 50% of the measurements at most sites are below detection).
- Concentrations are consistent for areas dominated by mobile sources (e.g., the Northeast and California), while isolated high concentrations generally coincide with significant point source emissions of benzene, such as refineries and coking operations.
- Sites that show unusually high concentrations with no clear emissions sources, or sites with concentrations that are very different from other sites (e.g., the yellow circles in the map above), might be further investigated to determine the cause.

Spatial Patterns – Maps

1,3-Butadiene Concentrations 2003–2005

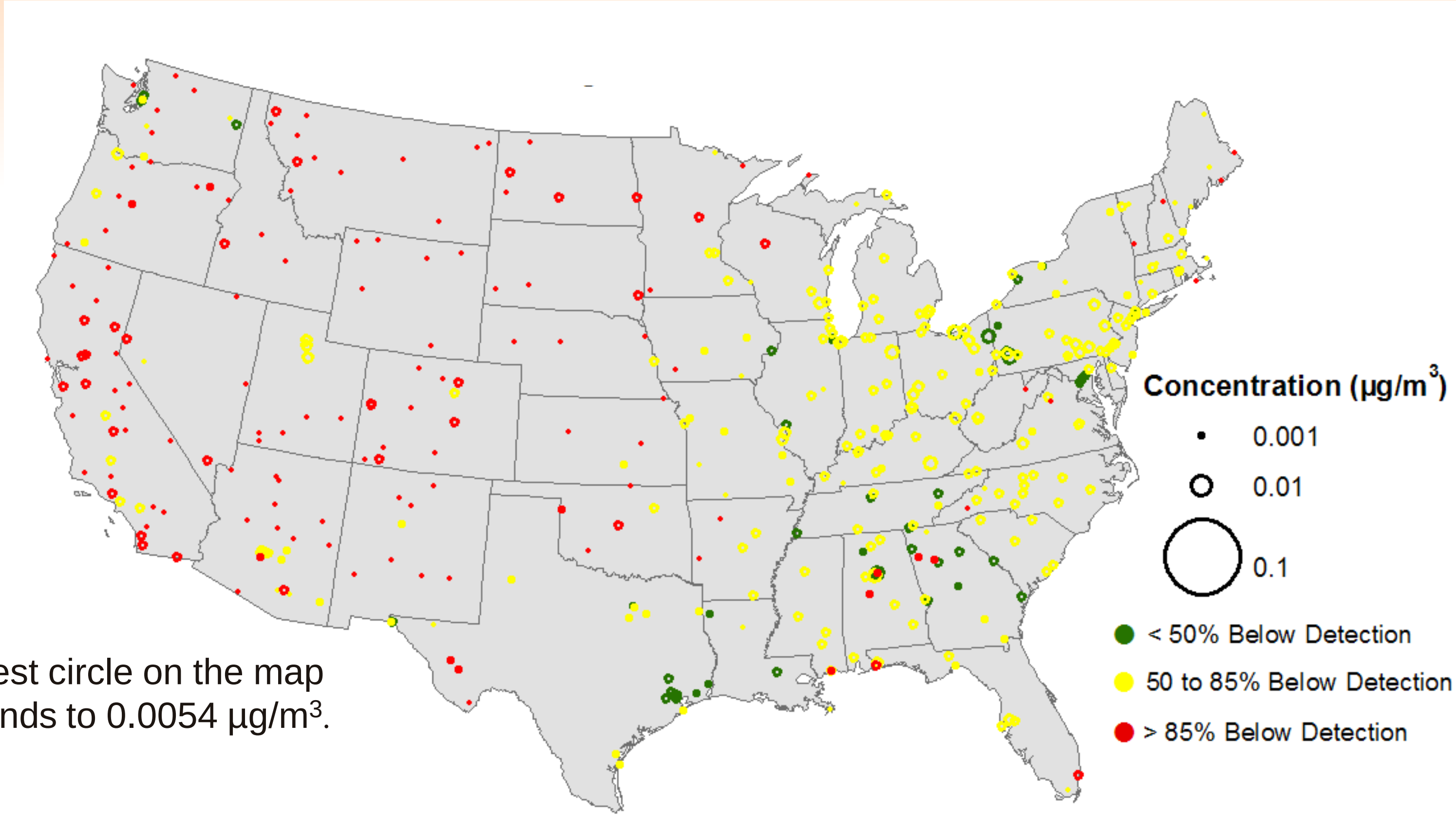


The largest circle on the map corresponds to 6.6 µg/m³.

- The ability to obtain 1,3-butadiene concentration measurements above the MDL across the United States varies (note all the red circles and their varying sizes).
- Higher concentrations generally coincide with locations of known point source emissions.
- Differences in monitoring methods and methods application have resulted in large differences in reported MDLs across the United States.

Spatial Patterns – Maps

Arsenic $PM_{2.5}$ Concentrations 2003–2005

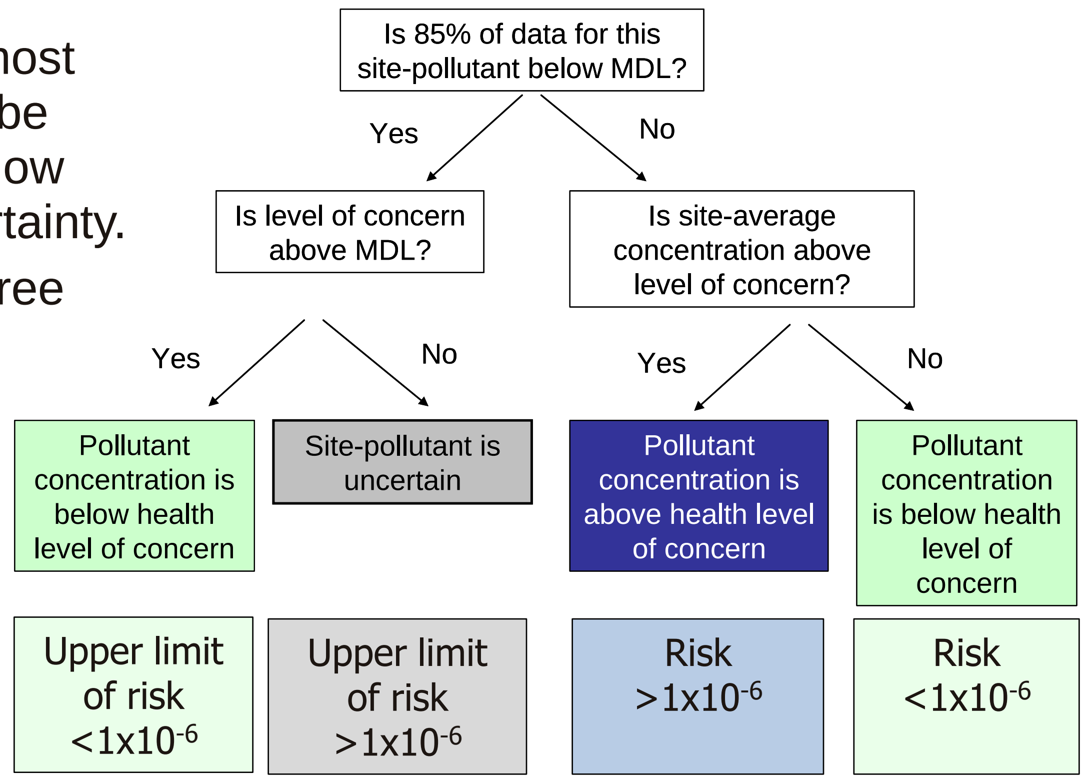


The largest circle on the map corresponds to 0.0054 µg/m³.

- Arsenic concentrations are widely measured across the United States, and the entire range of data availability is observed, from more than 50% of data above detection to less than 15% above detection.
- Significant MDL differences between networks make determining spatial patterns difficult.
- In general, concentrations are higher and more often above detection in the eastern half of the country.

Risk Screening Approach

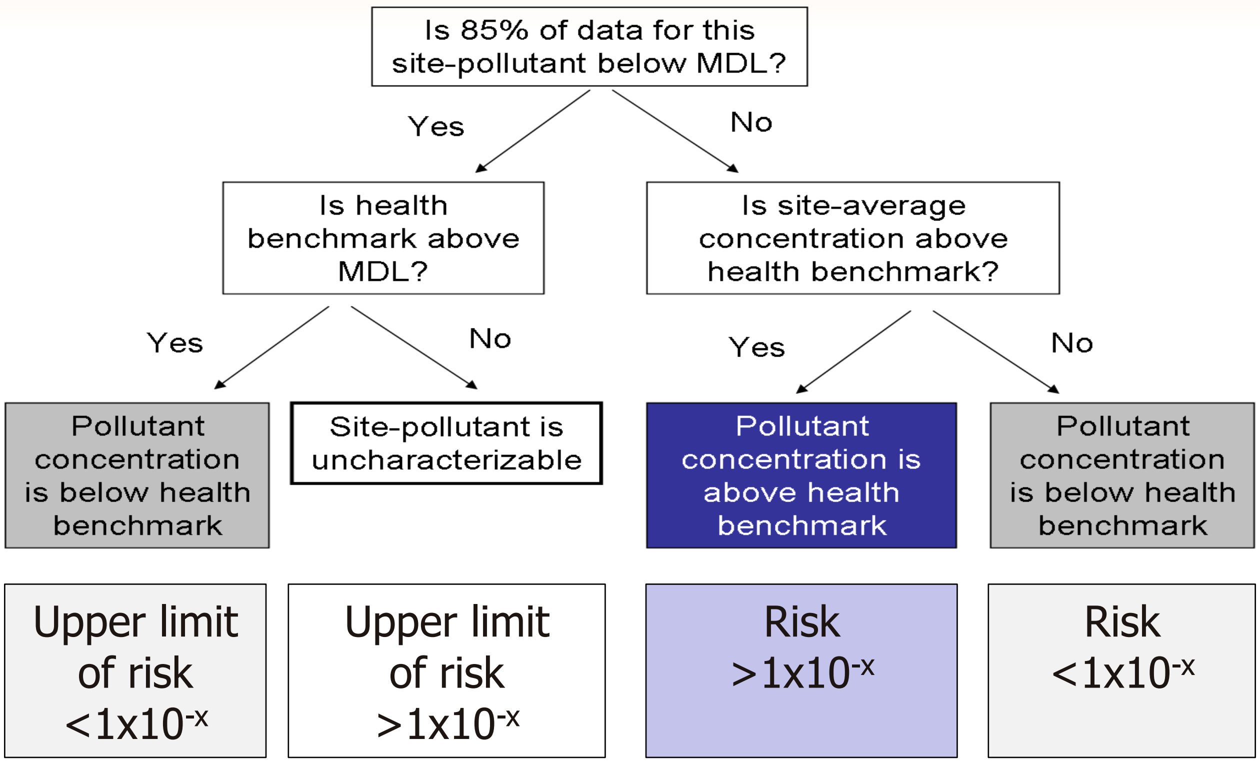
- For this first level of screening, site average concentration data from 2003–2005 were used to identify the number of sites at which a pollutant was definitively above or below the relevant EPA OAQPS chronic exposure concentration associated with a 1-in-a-million cancer risk as found at http://www.epa.gov/ttn/atw/toxsource/summary.html. Results are ranked by screening level.
- Air toxics were also noted if most site concentrations could not be characterized as above or below the relevant risk level with certainty.
- The figure shows a decision tree for performing risk screening.



The % of data below MDL listed in the first box may need to be stricter or less strict to meet your DQOs.

Health Effects Assessments

Risk Screening



Where 10^{-x} is user defined

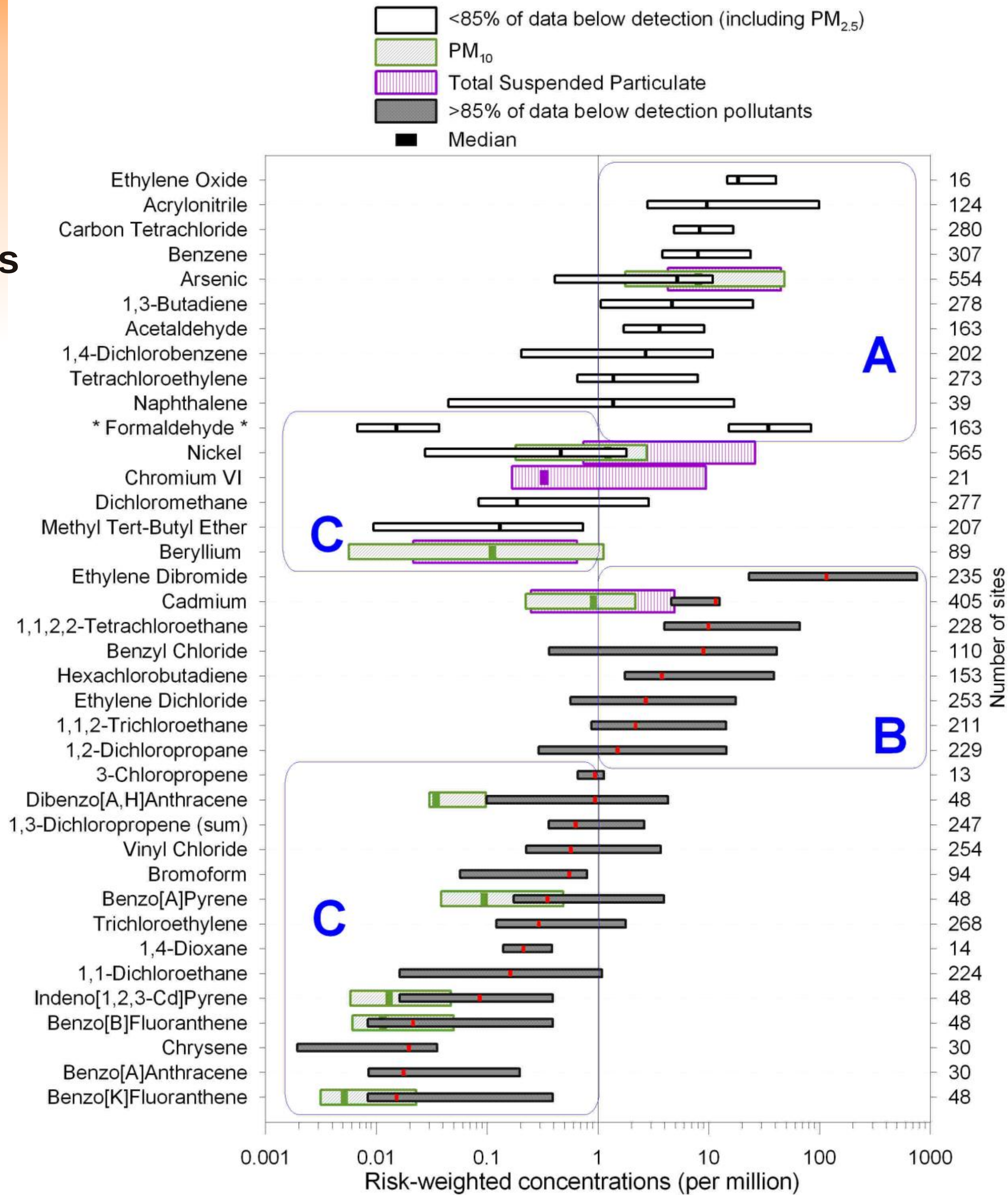
Health Effects Assessments

Risk-weighted concentrations

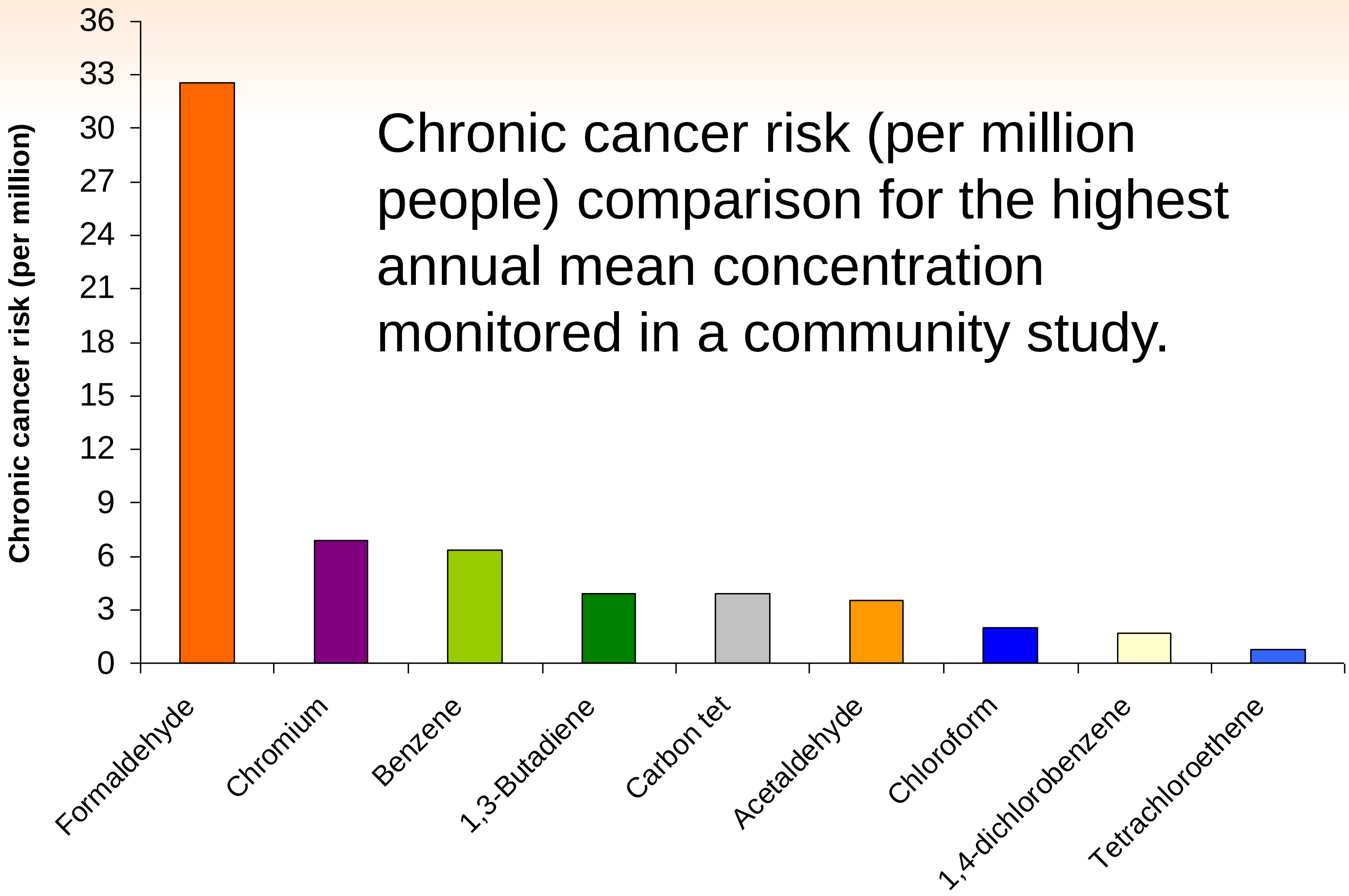
A. Pollutants with a majority of sites with risk estimates > 1-in-a-million risk level.

B. Pollutants with most of the data < MDL, but detection limits above the 1-in-a-million risk level.

C. Pollutants with the majority of monitoring sites reporting concentrations < the 1-in-a-million risk level, including those usually above and below MDL.



Health Effects Assessments



Summary

Check List for Ways to Characterize Air Toxics

Temporal Characterization

- The general procedure for investigating temporal patterns is the same for all temporal aggregates.
  - Prepare valid concentration and normalized temporal aggregates and summary statistics.
    - Normalization allows comparison between sites and pollutants even if absolute concentration values vary widely.
    - Keep track of the amount of data below detection.
  - Plot data with notched box plots or line graphs of multiple statistics (e.g., mean vs. 90th and 10th percentiles) with confidence intervals.
  - Characterize patterns by pollutant
    - Do patterns fit your conceptual model?
    - Are they statistically significant?
  - Investigate unexpected results.
- Day-of-week patterns – examine data availability by day of week.
  - If sufficient data exist for each day of the week, examine day-of-week patterns.
  - If insufficient data exist, weekday vs. weekend groupings can be used.
- Seasonal patterns – aggregate to the monthly level if sufficient data exist. Use quarterly averages if data are not sufficient or monthly patterns are too noisy.
- Compare what you have learned from the different temporal aggregates. Do conclusions make sense in the larger temporal picture?

Summary

Check List for Ways to Characterize Air Toxics

Spatial Characterization

- ❑ General spatial patterns
  - – Create site level average values by pollutant for the time period of interest. Make sure data are temporally comparable at all sites.
  - – Investigate spatial variability by calculating and graphing summary statistics of site averages. Results provide information about the magnitude of spatial variation.
  - – Visualize spatial variability by creating maps of the site-level average concentrations.
    - Results will provide more specific information about the spatial gradients of air toxics.
    - Including supplementary data, such as MDLs, remote background concentrations, and cancer and noncancer risk levels, provides context.
- ❑ Within- and between-city variation
  - – Calculate valid annual averages for each site within a city that has more than one monitor.
  - – Create notched box plots of annual averages by city.
- ❑ Hot and cold spot analysis
  - – Calculate valid annual averages for each site.
  - – Rank the averages in order of concentration.
  - – Using maps, compare sites with highest and lowest concentrations to all sites.
  - – Investigate data and metadata for the sites with highest and lowest concentrations. Do concentrations make sense based on the metadata and conceptual models?
- ❑ Urban vs. rural site analysis
  - – Verify the urban/rural designation of each site using Google Earth.
  - – Identify pollutant data availability and time period.
  - – Create a data set of pollutant/site combinations that are spatially and temporally representative.
  - – Plot valid 24-hr average data as notched box plots for neighboring urban and rural sites.
  - – Summarize the results and investigate sites that do not meet the conceptual model of an urban or rural site.

Summary

Check List for Characterizing Air Toxics

Risk Screening

- ❑ Create valid site average concentration data for the most recent years.
- ❑ Calculate the percentage of sites above the selected risk level and the percentage of data below detection.
- ❑ Follow the risk screening decision tree to identify the exposure risk for each pollutant.
- ❑ More advanced risk analyses should be performed by risk assessment professionals.

A Final Note on Data Below Detection

- Most air toxics have enough data below detection to cause uncertainties and/or biases in aggregated data if not handled properly.
- Note, however, that it is not valid to remove these data, because they are representative of true values on the lower end of the concentration spectrum; removal would cause even more significant positive biases.
- It is always important to know the amount of data below detection when looking at any data set. The effects of data below detection should be considered in all analyses.
- In national analyses, we did not draw conclusions when more than 85% of the measurements of a pollutant were below detection.